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Determination of Plutonium Present in Highly Radioactive Irradiated Fuel Solution by Spectrophotometric Method

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ABSTRACT

A simple and rapid spectrophotometric method has been developed to enable the determination of plutonium concentration in an irradiated fuel solution in the presence of all fission products. An excess of ceric ammonium nitrate solution was employed to oxidize all the valence states of plutonium to +6 oxidation state. Interference due to the presence of fission products such as ruthenium and zirconium, and corrosion products such as iron in the envisaged concentration range, as in the irradiated fuel solution, was studied in the determination of plutonium concentration by the direct spectrophotometric method. The stability of plutonium in +6 oxidation state was monitored under experimental conditions as a function of time. Results obtained are reproducible, and this method is applicable to radioactive samples resulting before the solvent extraction process during the reprocessing of fast reactor spent fuel. An analysis of the concentration of plutonium shows a relative standard deviation of <1.2% in standard as well as in simulated conditions. This reflects the fast reactor fuel composition with respect to uranium, plutonium, fission products such as ruthenium and zirconium, and corrosion products such as iron.

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1. Introduction

Mixed carbide fuel of 70% PuC and 30% UC is used as the driver fuel in the fast breeder test reactor (FBTR) at Kalpakkam, India. Spent fuel of various burn-ups from 25 GWd/t to 155 GWd/t, discharged from the FBTR with cooling periods of not less than 2 years, is reprocessed in a Compact Reprocessing of Advanced Fuel in Lead Shielded Cell (CORAL) facility. The

modified PUREX process [1–3] is followed, in which tri-n-butyl phosphate (30%) diluted with n-dodecane is employed as an extractant to recover Pu and U, leaving the bulk of fission products in a highly radioactive aqueous waste stream. A high-acid flowsheet condition [4] is adopted in order to obtain the required decontamination factor with respect to ruthenium, owing to its high yield in the fast neutron spectrum and the low cooling period of spent fuel after being discharged

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from a reactor. Samples generated at different steps of the solvent extraction process are analyzed for U, Pu, acidity, and fission product activities to understand the plant performance. Chemical methods are being followed for U analysis [5] and free acidity [6]. The alpha counting method was employed to determine the concentration of Pu in the plant samples generated at various steps during the reprocessing of spent fuel. This method is simple, rapid, and sensitive, but it requires the exact specific activity of the resultant Pu, which depends on the isotopic composition of the fissile material. As the half-life periods of ^{238}Pu ($t_{1/2} = 88$ years) and ^{240}Pu ($t_{1/2} = 6,563$ years) are less than that of ^{239}Pu ($t_{1/2} = 24,360$ years), small variations in the isotopic composition of ^{238}Pu and ^{240}Pu cause a wide range of changes in the alpha specific activity of Pu. Spent fuel from various fuel subassemblies with different isotopic compositions and burn-ups ranging from 25 GWd/t to 155 GWd/t are reprocessed in a CORAL plant. The alpha specific activity of Pu present in the irradiated fuel solution varies with respect to the burn-up and fuel subassembly. Hence, isotopic composition of the fuel material is determined first for obtaining alpha specific activity of the resultant fuel material, in order to follow the radiometric counting technique for analysis of plant samples. The increasing availability of powerful instrumental techniques such as isotopic dilution mass spectrometry [7,8], alpha spectrometry [9], and lead slowing down spectrometry has enabled the analysis of fissile content in the spent fuel discharged from a nuclear reactor. In general, isotope dilution mass spectrometry is employed for the determination of the isotopic composition of fissile material, and it involves the use of valuable reference materials and plutonium in the purest form. However, the time-consuming ion exchange chromatography technique is employed for the purification of Pu and U from fission products and minor actinides in the irradiated fuel solution for mass spectrometric studies. This step contributes considerably to high radiation exposure of the operating personnel due to the high level of fission product activities associated with spent fuel. However, the advantage of a lead slowing down spectrometer is that direct assay of isotopic fissile content in spent fuel is possible and this technique is not influenced by the intense gamma radiation background [10]. However, the above-said advanced techniques require sophisticated, expensive instruments and a skilled analyst. Hence, these techniques are employed for the analysis of a limited number of samples taken at key measurement points of the aqueous reprocessing process for the purpose of accountability. For samples with concentrations of Pu above the micromolar level, the absorption spectrophotometric method is considered to be a reliable technique for quantitative determination as well as detection of various oxidation states of Pu in the aqueous solution. The absorption spectrophotometric method reported in the literature for the determination of Pu concentration requires a suitable chromogenic agent [11] and the analyte should be in the pure form [12]. The objective of this study is to apply the direct spectrophotometric method for the determination of Pu content in the presence of major fission products such as ruthenium and zirconium, and a corrosion product (iron) from the spent fuel of a fast reactor. Hence, a tedious procedure involving the separation of Pu from complicated matrices prior to estimation is not required using

this technique. This method is very simple and less time consuming, the risk of radiation exposure is minimized, and it can be applied for analyzing radioactive samples generated in various steps of reprocessing of spent fuel.

2. Materials and methods

2.1. Chemicals and reagents

Chemicals of AR grade were used to prepare the standard solution for quantitative determination. Nitric acid (AR, Merck, Mumbai, India), potassium dichromate (AR, Merck, Mumbai, India), sodium hydroxide (AR, SD Fine Chemicals Limited, Mumbai, India), potassium hydrogen phthalate (AR, Merck, Mumbai, India), and potassium oxalate (AR, Merck, Mumbai, India) were used. Ruthenium nitrosyl trinitrate, zirconyl nitrate (AR, Lobachemie Pvt. Limited, Mumbai, India), and ferric nitrate (AR, Lobachemie Pvt. Limited, Mumbai, India) were used for the preparation of feed solution in simulated conditions. The ceric ammonium nitrate (AR, Lobachemie Pvt. Limited, Mumbai, India) required for this experiment was prepared by dissolving the required quantity in double-distilled water to the known volume. Plutonium oxide powder used in this study for the preparation of standard plutonium nitrate solution was of nuclear grade, and it was obtained by calcination of plutonium (IV) oxalate cake at 500°C after reprocessing of spent fuel discharged from the FBTR.

2.2. Instruments

A fiber-optic spectrophotometer with a wave length range of 300–1,100 nm, supplied by Ocean Optics, Dunedin, FL, USA (USB 4000 model), was used for all absorbance measurements during spectrophotometric determination of Pu concentration. An alpha scintillation counter supplied by Nucleonix (Hyderabad, India) was used for the determination of plutonium concentration by the alpha counting method.

2.3. Preparation of plutonium nitrate stock solution

All experiments with solid plutonium dioxide were performed in the glove box with extreme care. A weighed quantity of plutonium oxide was dissolved in a mixture of 11M nitric acid containing 0.1M hydrogen fluoride at $85\text{--}90^{\circ}\text{C}$ in a 100 mL Teflon beaker. The plutonium nitrate solution was purified from americium by employing the anion exchange separation procedure using Dowex 1×8 resin in a nitric acid medium [13]. The concentration of Pu in the purified stock solution was determined by the redox titrimetric method using fuming perchloric acid as an oxidizing agent.

2.4. Effect of ceric ammonium nitrate concentration on the oxidation of Pu (IV) to Pu (VI)

A known volume of diluted plutonium nitrate stock solution (700 mg/L) was added to a 5 mL standard flask to get a Pu concentration of 140 mg/L. Different amounts of ceric ammonium nitrate (0.5–3.0 mL of 1M concentration) were added to the Pu already placed in a 5 mL flask. The final

volume of this solution was made up to 5 mL using 1M nitric acid. Then these samples were subjected to absorption measurement in the wavelength range of 600–900 nm at a scan speed of 100 nm/s. The absorbance of Pu (VI) peak at around 830 nm was measured. The measured absorbance at 835 nm was employed for baseline correction.

2.5. Determination of Pu concentration using a calibration curve

Different quantities of Pu in 1M nitric acid were added to a 5 mL standard flask to get Pu concentrations in the range of 70–420 mg/L. Exactly 1.5 mL of 1M aqueous ceric ammonium nitrate solution was added, and the final volume was made up to 5 mL using 1M nitric acid. The absorbance of Pu (VI) at different concentrations was measured at 830 nm against a reagent blank solution containing nitric acid and ceric ammonium nitrate. The calibration curve was drawn by taking the average value of five similar measurements of each standard solution.

2.6. Study of interference from fission products in the determination of Pu concentration

A typical composition of the dissolver solution of FBTR spent fuel is as follows: [Pu], 30–35 g/L; [U], 15–20 g/L; [Ru], 0.6–0.97 g/L; [Cs], 1.3–1.5 g/L; [Fe], 0.3–0.4 g/L; [Zr], 0.7–1.0 g/L; and [HNO₃], 4–5M [14]. Concentrations of Ru and Zr in the spent fuel are expected to vary in the range from 10 mg/g to 18 mg/g of fuel depending on the burn-up and cooling time. Studies on the interference from major fission and corrosion products were carried out during direct spectrophotometric determination of Pu concentration in a nitric acid medium, using a simulated feed solution containing Pu (35 g/L) and U (20 g/L) with ruthenium, zirconium, and iron in a high concentration range envisaged in the dissolver solution of high burn-up and short-cooled spent fuel. The stock solution thus prepared was further diluted (a dilution factor of 200), and the sample was measured in the range of 600–900 nm at a scan speed of 100 nm/s after oxidation of all the valences of Pu to Pu (VI). Absorbance at around 830 nm was measured. Different solutions containing Pu in pure and simulated feed conditions along with the solution containing U [UO₂(NO₃)₂], zirconium [ZrO(NO₃)₂], ruthenium [RuNO(NO₃)₃], and ferric nitrate with the oxidant in a 1.0M HNO₃ medium were scanned from 600 nm to 900 nm, to get respective absorption spectra for each sample system. Similarly, absorption spectra of Pu (VI) in pure and simulated feed conditions were recorded at different time intervals under similar conditions, and all spectra were recorded.

2.7. Procedure for the determination of plutonium concentration in an actual plant sample

An aliquot of exactly 0.2 mL from the dissolver sample of spent fuel of burn-up 155 GWd/t, with a cooling period of 2 years, discharged from the FBTR was quantitatively transferred to a standard flask inside lead shielding and made up to 10 mL using 1M nitric acid. An aliquot of 1.25 mL of sample after the first dilution was taken into a 5 mL standard flask. Ceric ammonium nitrate (1.5 mL) was added and made up to 5 mL using 1M nitric

acid. Absorbance was measured at 830 nm against a blank solution. A baseline correction was made by subtracting absorption at 835 nm from that at 830 nm, and the concentration of Pu was obtained using Eq. (1):

$$[\text{Pu}] \text{ g/L} = [(A_{\lambda 830} - A_{\lambda 835})/462] \times 239 \times \text{df} \quad (1)$$

where A is the absorbance, and df the dilution factor.

2.8. Procedure for the determination of Pu concentration in an actual plant sample by alpha counting method

An aliquot from the dissolver sample was suitably diluted in an extraction vial, and the oxidation state of Pu in the diluted sample was converted to +4 by addition of sodium nitrite and adjusting feed acidity to 1.0M. The Pu in this sample was selectively extracted into 0.5M theonyl trifluoro acetone diluted in o-xylene by equilibrating the two phases in a vortex shaker for 20 minutes. Exactly 100 µL of organic theonyl trifluoro acetone layer loaded with plutonium was planchatted on hot SS discs and dried on a hot plate. The dried planchets were heated in a Bunsen flame to red hot and cooled. Alpha activity in the planchet was measured using an alpha scintillation counter. Pu concentration in the sample was calculated from alpha activity using the following equation:

$$[\text{Pu}] \text{ g/L} = (100/\eta) \times (\text{net mean counts/specific activity of Pu}) \times \text{df} \quad (2)$$

where η is the efficiency of the alpha counter and df the dilution factor.

3. Results and discussion

Pu ions in the nitric acid medium exist in (III), (IV), and (VI) oxidation states due to their disproportionation behavior. The advantages of a sharp absorption peak of Pu (VI) at 830 nm, large molar absorptivity compared with Pu (III) and Pu (IV), and lower interference of other ions in this wavelength region [15,16], direct spectrophotometric determination of Pu in VI oxidation state is preferable [17]. As molar absorptivity of PuO₂²⁺ decreases with increasing nitric acid concentration, nitric acid of 1–2M concentration is chosen as a medium due to the higher molar absorptivity value found at that concentration [18]. In the PUREX process of spent fuel reprocessing, if the concentration of nitric acid is 1M, the samples can be analyzed without adjusting the acidity. Ceric ammonium nitrate was employed for adjusting oxidation states of Pu (III) and Pu (IV) to Pu (VI), and oxidation of Pu takes place as described in Eqs. (3) and (4). The nitrous acid present in the nitric acid medium consumes ceric ions, and this reaction is described by Eq. (5). Hence, ceric ammonium nitrate in excess of the stoichiometric requirement was employed for quantitative oxidation of lower valences of Pu to Pu (VI).

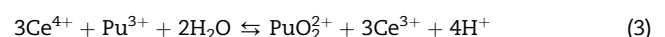
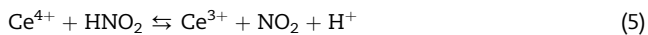
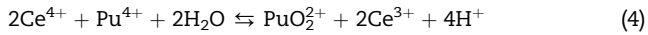


Table 1 – Effect of ceric ammonium nitrate concentration on the determination Pu concentration.^a

Samples	Volume of ceric ammonium nitrate added (mL)	[Pu] _{added} (mg/L)	[Pu] _{determined} (mg/L)	% difference
1	0.5	140	131.8	5.9
2	1.0	140	136.0	2.8
3	1.5	140	141.5	1.0
4	2.0	140	138.3	1.2
5	2.5	140	143.7	2.6
6	3.0	140	144.3	3.0

^a Number of measurement for single sample is 3 ($n = 3$); molar absorption coefficient is 462 L/(mol cm); medium 1M HNO₃ in 5 mL standard flask.



The analytical results summarized in Table 1 indicate that concentration of Ce (IV) is required to be maintained at 0.3–0.4 mol/L for the determination of Pu concentration in the sample, with a relative deviation of < 1.2%. If the concentration of the ceric ammonium nitrate is < 0.3 mol/L, it results in a lower value of absorption and a negative bias is obtained on the measured concentration of Pu. The probable reasons for the negative bias in the Pu concentration are the insufficient oxidation of lower valences of Pu to PuO₂²⁺ and the existence of equilibrium more toward the reactant side under this condition. Hence, further increases in the concentration of ceric ion in the solution are required for the quantitative oxidation of Pu. Based on experimental results, 1.5–2.0 millimoles of ceric nitrate are optimized for the quantitative oxidation of ≤ 2 mg of Pu under experimental conditions. When the concentration of ceric ion is increased further, a slight shifting of the baseline was observed. This may be due to the formation of new species consisting of cerium (IV)–cerium (III) dimers [19]. Hence, the concentration of 0.3–0.4 mol/L ceric ions is sufficient to oxidize all the lower valences of Pu quantitatively to PuO₂²⁺ in the aliquot containing ≤ 2 mg of Pu in a 5 mL volumetric flask.

Table 2 shows the results of Pu determination in standard plutonium nitrate solution (25 g/L) as well as in a simulated condition corresponding to the dissolver composition in a CORAL plant. Simulated sample contains 35 g/L Pu and 20 g/L U in addition to ruthenium (1.0 g/L), zirconium (1.0 g/L), and iron (0.4 g/L). Results obtained by radiometry as well as direct

spectrophotometric method indicate good agreement with the relative standard deviation of < 1.2% during the determination of Pu concentration in pure and simulated conditions. Results shown in Table 2 also indicate that analysis of Pu by this method has no significant interference from major impurities at envisaged concentration limits in spent fuel discharged from a fast reactor studied under experimental conditions.

To assess the analytical potential of the method, determinations were made for a set of measurements of Pu in 1M nitric acid medium under optimum conditions. As shown in Fig. 1, the measured absorbance was plotted against the known concentrations of Pu. A linear relationship was found for samples containing Pu in a concentration range from 70–420 µg/mL, with a correlation coefficient of 0.995. The molar absorptivity obtained from the slope was 462 L/(mol cm).

The oxidation state of PuO₂²⁺ was monitored as a function of time, and it was extended up to several hours. Fig. 2 shows the combined absorption spectra of Pu after oxidation to PuO₂²⁺ recorded at different time intervals (20 minutes, 20 hours, and 40 hours), with the sample aliquot containing plutonium nitrate in pure and simulated conditions. The Pu (VI) absorption value at around 830 nm in Fig. 2 in standard as well as simulated conditions has not changed with respect to time. Table 3 shows the results of the determination of Pu concentration using absorbance of the Pu (VI) peak at around 830 nm. The relative standard deviation of concentration of Pu, determined in repeated analysis ($n = 3$) by the proposed method in standard as well as simulated conditions at different time intervals, was found to be ±1.0%. These results indicate that +6 oxidation state of Pu is stable for > 24 hours in

Table 2 – Results of analysis of Pu in standard and simulated feed conditions envisaged in FBTR spent fuel.

Samples	[Pu] in standard condition (g/L)		[Pu] in simulated condition ^a (g/L)	
	Spectrophotometric determination	Radiometric determination	Spectrophotometric determination	Radiometric determination
1	20.13	20.15	35.67	35.73
2	20.09	20.21	34.82	35.49
3	19.88	20.17	35.52	35.82
4	19.75	20.48	34.69	35.33
5	20.05	20.34	35.03	35.46
Mean	19.98	20.27	35.15	35.57
RSD	0.72	0.58	1.10	0.51

FBTR, fast breeder test reactor; RSD, % relative standard deviation.

^a Simulated feed solution contains [Pu] → 35 g/L, [U] → 20 g/L, [Ru] → 1 g/L, [Zr] → 1.0 g/L, and [Fe] → 0.4 g/L.

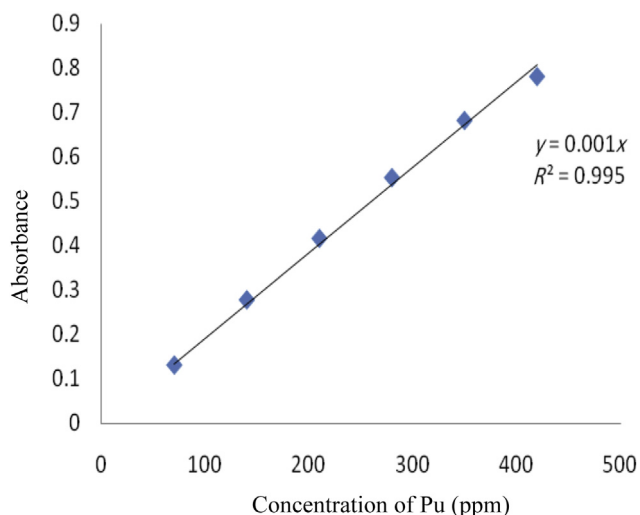


Fig. 1 – Calibration curve for the concentration determination of Pu (VI) in 1M HNO₃ containing 0.3M (NH₄)₂Ce(NO₃)₆.

1.0M nitric acid under experimental conditions. The value of absorbance measured for the same sample system after 24 hours indicates that the presence Ru, Zr, and iron do not interfere with the quantitative determination of Pu. Fig. 3 indicates combined individual absorption spectra of sample systems containing plutonyl nitrate, uranyl nitrate, zirconyl nitrate, ruthenium nitrosyl trinitrate, and ferric nitrate along with Pu in simulated conditions. The presence of impurities studied under experimental conditions did not show any significant absorbance in the wavelength region around 830 nm.

Table 4 shows the Pu concentrations in real plant samples determined by the proposed method and the radiometric counting technique. These values are in good agreement, indicating that the presence of minor actinides, lanthanides, and other fission products in the irradiated fuel solution do not contribute any significant interference in the analysis of

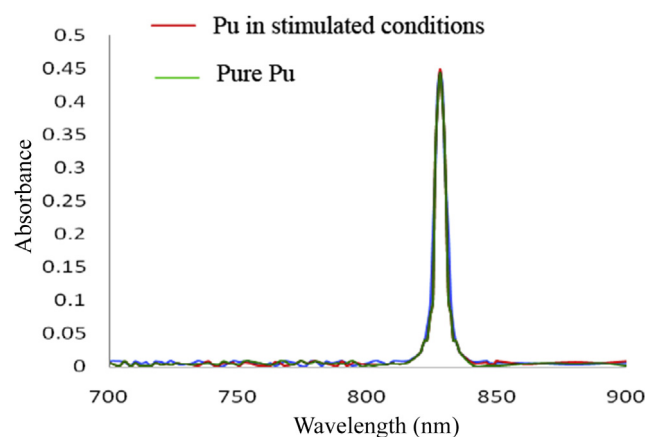


Fig. 2 – Combined absorption spectra of Pu (VI) in pure and simulated solution condition in 1M HNO₃ containing 0.3M (NH₄)₂Ce(NO₃)₆ at different time intervals (20 minutes, 20 hours, and 40 hours).

Table 3 – Results of analysis of Pu in standard and simulated conditions at different intervals of time.

Time	Pu in standard condition ^a		Pu in simulated condition ^b	
	Absorbance after baseline correction	[Pu] (g/L)	Absorbance after baseline correction	[Pu] (g/L)
20 min	0.456	11.79	0.459	11.87
20 hr	0.457	11.82	0.451	11.67
40 hr	0.452	11.69	0.449	11.61

^a Standard Pu stock solution contains [Pu] = 11.57 g/L in 1M HNO₃ medium. The stock solution was diluted 50 times before recording absorbance spectrum under experimental conditions.

^b Simulated Pu stock solution contains [Pu] = 11.57 g/L, [Zr] = 1.0 g/L, [Ru] = 1.0 g/L, and [Fe] = 0.5 g/L in 1M HNO₃ medium. The stock solution was diluted (dilution factor of 50) before recording absorbance spectrum under experimental conditions.

Pu by this method. Hence, this method can be employed for monitoring Pu concentration in highly radioactive samples generated at various steps during the aqueous reprocessing of spent fuel from a fast reactor.

An analytical method using a conventional spectrophotometer to determine Pu concentration in highly radioactive samples was developed as an alternative method. The experimental results indicate that the absorbance has a linear relationship with the concentrations of Pu in the range of 70–400 µg/mL in nitric acid (1M) containing 0.3–0.4M ceric nitrate as an oxidant, with a precision and accuracy of $\pm 1.1\%$. This method is relatively simple and rapid, and can be applied successfully for the determination of Pu concentration in a sample with complex matrices of fast reactor spent fuel composition with reduced collective doses. This method does not need any purification step during the determination of Pu concentration from fission products and minor actinides. Handling of various analytical wastes containing chloride- and sulfate-bearing corrosive chemicals is an important issue in reprocessing plants. However, analytical waste generated

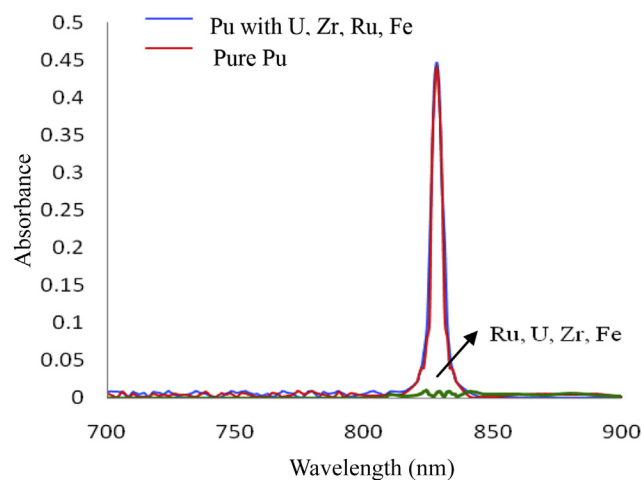


Fig. 3 – Combined absorption spectra of Pu (VI) in pure, simulated condition and individual absorption spectra of zirconium, ruthenium, and ferric nitrate solution without Pu (VI) in 1M HNO₃ containing 0.3M (NH₄)₂Ce(NO₃)₆.

Table 4 – Concentration determination of Pu in an actual dissolver solution.

Sample number	Absorbance at 830 nm	Absorbance at 835 nm	Absorption after baseline correction	[Pu] ^a (g/L)	
				Spectrophotometric method	Radiometric method
1	0.354	0.019	0.335	34.66	35.67
2	0.351	0.008	0.343	35.49	35.31
3	0.347	0.003	0.344	35.59	35.50

^a Dissolver solution of spent fuel of 155 GWd/t with a cooling period of 2 years was used; absorbance was measured after diluting samples (dilution factor of 200); molar absorption coefficient = 462 L/(mol cm); 1.5 mL 1M ceric ammonium nitrate was added; the medium was 1M HNO₃ in a 5 mL standard flask.

by this technique does not introduce any corrosive chemicals, and its composition is identical to the plant solution. Hence, conventional solvent extraction methods can be employed for the recovery of valuable fissile materials from the waste solution generated by this method.

Conflict of interest

The authors declare no conflict of interest.

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